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DRAFT EPA RECOMMENDED PRACTICE FOR NAMING I/M CALIBRATION GAS

September, 1981

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Abstract

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1.0 BACKGROUND

An Inspection and Maintenance (I/M) program is a state or locally run program in which registered vehicles are required to obtain and pass a tailpipe emission inspection once per year. Vehicles that have tailpipe emissions greater than state or locally established emission standards are required to obtain maintenance to pass that standard. The emission test (called a "short test") can be conducted by the state (or locality) or a contractor to the state, and this is referred to as a "centralized program". The emission test can also be conducted by private garages which are licensed by the state. This latter system is called a "decentralized" program. Twenty-nine states are expected to have operating programs by Janurary 1, 1983, however, many of these programs will commence before that date. At this time, 11 states are expected to have decentralized programs, 16 states are expected to have centralized programs, and two states are undecided.

The primary inspection and diagnostic tool of these I/M programs is a Non-Dispersive Infrared (NDIR) analyzer, which is capable of determining the concentrations of hydrocarbons (as hexane) carbon monoxide, and in some cases carbon dioxide in raw vehicle exhaust. These analyzers, however, need periodic maintenance to keep their accuracy, as operator misuse, or changes in pressure, temperature, and other operating variables can render them inaccurate.

Many analyzer manufacturers recommend a periodic check of their analyzers with an accurate calibration gas. State or local I/M program regulations will also

require a periodic check. This check is performed by flowing a known concentration of calibration gas into the analyzer and determining whether the analyzer is reading this calibration gas correctly. If it is not, then a simple adjustment (i.e., a calibration) of the analyzer can usually be performed which will result in the analyzer being accurate again. However, the accuracy of the calibration gas used is also important in determining analyzer accuracy with this maintenance check. If the labeled concentration of the calibration gas is significantly different than the concentration in the cylinder, the analyzer could become significantly misadjusted. An operator who had performed the calibration would be unaware that he/she had actually misadjusted the analyzer, since he/she trusted the label on the calibration cylinder to be correct.

1.1 EPA Regulations Concerning Calibration Gas Accuracy

The EPA recently promulgated Emission System Performance Warranty Regulations for 1981 and later vehicles which entitle a vehicle owner to emission-related repairs at the manufacturer's expense if, among other things, the vehicle fails an "approved" emission short test. One of those conditions is that the analyzer used to conduct the emission short test must be checked with gases* "traceable to NBS standards ±2%" at least once per week (Section 85.2217, page

* Note: There are no CO_2 emission standards in the Emission Performance Warranty, consequently, the Warranty accuracy specification of ±2% traceable to NBS does not apply to CO_2. Also, since there are no NBS standards for hexane, the Warranty accuracy specification of traceable ±2% to NBS cannot be met on an analyzer calibrated with hexane only.

34808. The relevant portion of this page is provided in Appendix 1 to this document). There are other requirements for these gases in the Warranty; however, these are beyond the scope of this section and will be addressed in Section 2.3.1. The EPA thinks that many states implementing I/M programs will want to make Warranty protection available to consumers participating in their I/M programs. These states will try to make sure that the gases used to periodically calibrate analyzers used in the I/M programs meet the Warranty requirement of having an accuracy of ±2% to NBS standards. However, there are some practical problems associated with this accuracy requirement which are discussed in the following paragraphs.

1.2 Practical Problems With Warranty Accuracy Requirement

States might think that they have only to order calibration gases for their analyzers that have been certified by the manufacturer to be "traceable to NBS standards ±2%" to be ensured of meeting the accuracy requirement in the Warranty. However, the most conscientious gas manufacturers are very hesitant to label cylinders of calibration gas that they have analyzed with the phrase "±2% to NBS standards", as they point out that there is currently no clear-cut definition of "traceable" to NBS stanards. They explain that traceability implies a system of analytical procedures and documentation of data that is used to express the concentration of a particular gas relative to a standard gas. These analytical procedures and methods of handling data may vary significantly between manufacturers, causing differences in the concentrations of identically labeled calibration gases made by different manufacturers or even by the same manufacturers. I/M calibration gas users would find it

difficult to detect these differences and identify which gas cylinders were correctly labeled, with the possible exception of the I/M managers if they maintain a sophisticated gas analysis program of their own.

1.3 EPA Efforts to Help States Meet Warranty Requirement for Gas Accuracy

In order to improve the general quality of I/M programs, and to help states in meeting the accuracy requirement of the Warranty with respect to calibration gas used to check emission analyzers, the EPA has published this Recommended Practice which states can require gas manufacturers to follow in naming and labeling calibration gas for the I/M programs in those states. A state requirement would be imposed directly by the state in its own purchases of gas and/or indirectly by establishing rules and regulations which require other I/M gas users (contractors or licensed inspection stations) to buy only gas that the manufacturer certifies was named and labeled according to this Recommended Practice.

A special effort has been made to make these procedures workable from a scientific gas manufacturer's viewpoint. A meeting was held between the gas manufacturing industry, the National Bureau of Standards and the EPA to agree on the original framework of the procedures. Manufacturers have also been allowed to comment on the draft forms of the Recommended Practice: many of their comments have been incorporated into the procedures. The end result is a Recommended Practice which should contribute significantly to overall I/M program accuracy and fairness.

2.0 INTRODUCTION

2.1 I/M Calibration Gas Users

2.1.1 Centralized Programs

In a centralized I/M program where the official I/M short test is conducted in state or contractor operated centralized test facilities only, states are likely to require that only those analyzers in the centralized test facilities be checked at least once per week with an accurate calibration gas. Most states operating centralized programs will not require garage owners who have purchased analyzers to help them in the repairs of vehicles failed from the I/M programs to perform periodic calibration checks on their instruments. Therefore, analyzer operators in the centralized facilities will be the primary users of calibration gas in a centralized program. The exception to this situation is where a state running a centralized program licenses certain garages for the reinspection function (New Jersey, for example). In this case, the state will likely require reinspection garages to perform a periodic calibration check of the garage analyzer with an accurate calibration gas, also.

2.1.2 Decentralized Programs

In decentralized programs, there are likely to be two different categories of I/M calibration gas users. The first are the garages licensed by the state to perform emission inspections. States are likely to require that these garages

perform a periodic check of the garage analyzer with an accurate calibration gas. Also, decentralized programs will have official auditors who periodically visit each facility to determine (among other things) if the emission analyzers are accurate. Part of the auditor's job will be to check the facility's analyzer with state audit gas, to provide a double check against the facility's gas.

Many states are requiring their auditors to use calibration gases with accuracies of ±1% to NBS standards rather than the accuracy requirement of ±2% which is specified for weekly calibrations in the Warranty. Since some states have proposed regulations which would require auditors to use calibration gas which is traceable ±1%, included in this Recommended Practice are procedures which will allow gas manufacturers to name certain audit gases to within ±1% of NBS standards.*

Decentralized programs are expected to use more calibration gas than centralized programs. This is because decentralized programs consist of many small neighborhood garages performing a few emission inspections each, where a centralized program consists of a few high-throughput inspection facilities. Consequently, there are more analyzers in a decentralized program, each requiring the same periodic calibration checks as the fewer number of analyzers used in a centralized program.

* The one exception is an I/M calibration cylinder which contains both CO_2 and CO. The best accuracy specification on this cylinder named according to the Recommended Practice is ±1.5%. This issue is discussed further in Section 2.2.2 and Appendix 3.

2.2 Components of I/M Calibration Gases

A state has several options in determining how many and what components are in the calibration cylinders which are bought for calibrating analyzers in that state. The Recommended Practice generally does not limit the scope of these options: within certain limits as discussed in this section, there should be no difference in the quality or accuracy of gases in each option if the components are named in accordance with the procedures described in this Recommended Practice.

2.2.1 Carbon Monoxide and Propane

States must first examine what components are needed in a calibration cylinder(s) to ensure that inspected vehicles are accurately passed and failed. Some I/M programs are being implemented with a carbon monoxide (CO) cutpoint only.* The state may feel that analyzers therefore only have to be accurate at reading a vehicle's CO emissions, and determine that a calibration cylinder of CO is sufficient to ensure this accuracy. This determination is consistent with the Emission Performance Warranty. However, the EPA recommends that a state with a CO-only program require inspectors to calibrate their analyzers with propane as well as CO, since a mechanic performing repairs on a vehicle can use a vehicle's HC emissions to diagnose problems

* Some urban areas that are in non-attainment for CO but not for ozone will implement an I/M program which uses CO cutpoints only. The state of North Carolina is operating an I/M program which is in the voluntary inspection and maintenance phase of implementation which has cutpoints for CO only.

that may be causing a significant loss in fuel economy for that vehicle, and the costs of calibrating an analyzer with propane as well as CO are not significantly greater than the costs of calibrating an analyzer with CO only.

Most I/M programs will be implemented with CO and HC cutpoints. These states therefore are likely to require all the analyzers used for inspections in that state to be calibrated with both CO and propane.* The most convenient cylinder for them to order will be a three-blend cylinder of CO and propane in nitrogen. Some states may wish to order separate cylinders of CO in nitrogen and propane in nitrogen on the theory that there is "interference" between CO and propane in nitrogen such that both components appear to have slightly higher concentrations than they would if they were in separate cylinders. [However, the National Bureau of Standards (NBS) has studied the level of interference between CO and propane in typical I/M calibration gas concentrations, and determined that the interference effects are very slight.**] Consequently, little accuracy is gained by using two binary blend calibration gases (i.e., CO in nitrogen and propane in nitrogen) than by using a single tri-blend calibration gas (i.e., CO and propane in nitrogen).

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* Hexane might be used sometimes instead of propane. Hexane is discussed in Section 2.2.3.

** [Reference to not-yet-conducted NBS study.]

2.2.2 Carbon Dioxide

Some I/M programs will have carbon dioxide (CO_2) cutpoints for vehicles as well as HC and CO cutpoints. Checking for the amount of CO_2 in a vehicle's exhaust helps the state to determine whether there are significant leaks in a vehicle's exhaust system which are causing dilution of exhaust gases.

The Recommended Practice contains procedures which will allow gas manufacturers to incorporate CO_2 into I/M calibration gas mixtures and demonstrate traceability $\pm$2% to NBS of all components used. However, traceability better than $\pm$1.5% cannot be attained for these mixtures because of interference effects between CO_2 and CO. These and other considerations are discussed in the following paragraphs.

Inspection analyzers use infrared absorption principles to detect the concentrations of propane, CO, and CO_2 in vehicle exhaust. These gases absorb infrared radiation at different wavelengths, consequently the analyzer can, for the most part, differentiate completely between each gas. However, the wavelengths of absorption of CO and CO_2 are very close to each other. This has the effect of making some infrared analyzers slightly inaccurate at reading CO in the presence of CO_2, because they actually count a small portion of the CO_2 in the analysis of CO (but not vice versa).* This phenomenon is known as interference.

* The ability of infrared analyzers to read these components discreetly is a function of the quality of filters used in the analyzers.

Laboratory-type infrared analyzers which gas manufacturers will likely use to name CO in an I/M calibration cylinder containing CO_2 and propane are capable of keeping interference to minimum levels. The Recommended Practice requires gas manufacturers to keep the level of CO_2 interference in CO to less than .5% of the CO concentration when naming CO in an I/M calibration cylinder containing CO_2. Also, the Recommended Practice requires gas manufacturers to use tighter tolerances in naming I/M calibration cylinders containing CO_2. The small amount of additional interference error present when CO_2 is used requires these tighter tolerances so that all components meet the $\pm$2% to NBS accuracy requirement. However, the tolerances within the Recommended Practice have not been tightened to such a degree that traceability $\pm$1% for a mixture containing CO_2 and CO could be assured. Consequently, $\pm$1.5% is the best specification for this mixture attainable with this specification. A more complete discussion of how these accuracy specifications are arrived at is presented in Appendix 3.

Regardless of how accurately the calibration gases are named by laboratory-type infrared analyzers used by gas manufacturers, inspection analyzers are still likely to exhibit small interference effects.* A recent study by EPA determined the CO_2 interference levels in several common inspection analyzers. The results of the study are presented in Table 1.**

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* Another question raised by interference effects of CO_2 on CO is: What is the effect of calibrating an analyzer with a calibration cylinder containing CO and CO_2 on a vehicle's apparent CO emissions? If an analyzer's CO response is calibrated with a CO cylinder containing CO_2, the analyzer will be set at slightly lower than the actual CO concentration in the calibration cylinder because the analyzer will be responding to a small amount of CO_2 also. Since the analyzer's CO response will be set slightly lower, it will read a vehicle's CO emissions at a slightly lower level, thereby making a given short test slightly less stringent than it would have been had a CO cylinder that did not contain CO_2 been used for the calibration.

** "Operational Evaluation of Vehicle Exhaust Emission Inspection Analyzers", Volume 1, Contract # 68-03-2747, EPA 460/3-80-019.

Table 1

Combined % Full Scale+
HC and CO Responses of
Analyzers to 15% CO_2

Analyzer	% Combined F.S. Response
A	0.0%
B	1.74%
C	2.04%

+ The combined interference levels reflect the percentage full scale responses of the HC and CO meters to CO_2 gas. The percentages were added to get a "combined" response.

Based on the data in Table 1, it is probably better for an I/M inspector to check the CO response of an analyzer without using a CO cylinder that contains CO_2. If a state determines that CO_2 must also be used, then the CO_2 should be in a separate cylinder from the CO (i.e., one cylinder of CO and propane in nitrogen, the other cylinder CO_2 in nitrogen). If the state determines that the CO_2 must be in the same cylinder as the CO, the state should select the lowest CO_2 concentration acceptable to maintain the analyzer's CO_2 accuracy. This will minimize the interference effects of CO_2 on CO.

2.2.3 Hexane

Idle emission inspection analyzers, when determining the amount of hydrocarbons (HC) in vehicle exhaust, are really measuring the amount of hexane (actually n-hexane) in vehicle exhaust, plus some fraction of the

remaining hydrocarbons which appear to be partially hexane because of interference effects. The assumption inherent in the measurement technique is that the quantity of actual hexane plus other hydrocarbons which appear to be partially hexane due to interference is roughly proportional to the total quantity of all of the various types of hydrocarbons.

Because analyzer readouts are based on apparent hexane concentrations in vehicle exhaust, hexane is in theory the best gas with which to calibrate the HC portion of the analyzer. However, there are several problems associated with hexane which make it impractical as an inspection analyzer calibration gas, except under carefully controlled conditions.

First, there are no NBS standards for hexane. This means that the accuracy specification of "traceable $\pm$2% to NBS" is by definition impossible for hexane. However, that does not necessarily mean that one cannot obtain highly accurate hexane calibration gases. There are scientific gas manufacturers who have the resources to blend and name hexane accurately.

Second, hexane is a "sticky" molecule, and therefore has a tendency to cling to the sidewalls and interior fittings of a cylinder if the cylinder is not periodically agitated and/or heated. If sticking occurs in a cylinder of hexane, the concentration of hexane in the cylinder changes as the cylinder is used, since the diluent (balance gas) will flow from the cylinder first, leaving the hexane behind. Agitation of the cylinder by rolling it, and heating of the cylinder can significantly reduce this problem.

Lastly, hexane is much more expensive than propane to use as a calibration gas because of the problems in handling and blending it. Nonetheless, it still has potential uses in an I/M program. For example, because propane is usually used instead of hexane as a calibration gas, analyzer manufacturers must develop correction factors for their analyzers to convert a propane reading on the analyzer to a hexane reading. This correction factor can change slightly if the analyzer is roughly handled. A hexane calibration cylinder is needed to check or re-establish this correction factor periodically. Arizona and California I/M programs are currently using hexane to check analyzer correction factors.

2.2.4 Diluents (Balance Gases)

Throughout this report we have assumed that calibration gases would be blended with nitrogen as a diluent or balance gas. Nitrogen is the easiest gas to use as a diluent from a production standpoint since it is readily available in very pure forms.

Air could also be used as a diluent, however, gas manufacturers cannot use room air or ambient air because of the impurities present in these sources of air which could cause errors in the blending and naming processes. In order to use air as a diluent, gas manufacturers must buy pure nitrogen and oxygen and blend it together prior to filling I/M calibration cylinders. This process adds to the production costs for I/M calibration gases, therefore, most states will order I/M calibration gases which use nitrogen as a diluent.

2.3 Concentrations of I/M Calibration Gases

2.3.1 Emission Performance Warranty Requirements

In addition to the accuracy requirement for gases used to check emission analyzers (i.e., ±2% to NBS standards) the Warranty also requires the calibration gas to be within certain concentration ranges. The limitations are that the calibration gas must have concentrations of between -50% and +100% of the state emission standards if the state adopts the numerically minimum emission standards specified in the Federal Warranty Regulations, or have concentrations between these numerically minimum standards and the state selected emission standards if the state selected emission standards are numerically higher than the minimum emission standards. The minimum emission standards specified in the warranty are, depending on the short test procedure used, either 1.0% CO and 200 ppm hexane HC or 1.2% CO and 220 ppm hexane for HC. If a state selects emission standards of 1.0% CO and 200 ppm hexane, the concentration of calibration gas used to periodically check the analyzers must be between 0.5% and 2.0% for CO, and between 100 ppm and 400 ppm hexane (or 200 ppm and 800 ppm propane) for the emission short test to meet the terms of the Emission Performance Warranty. Alternately, if a state selects emission standards of 4.0% CO and 400 ppm HC (the highest standards any state is likely to adopt for 1981 and later vehicles), the concentration of calibration gas used to periodically check the analyzer must be between 1.0% and 4.0% for CO, and between 200 ppm and 400 ppm hexane for HC (or 400 and 800 ppm propane). See Table 2. The lower limits of 1.0% CO and 200 ppm hexane could be 1.2% CO and 220 ppm hexane if a different test procedure is used.

Table 2

Example of Calibration Gas Requirements
for 207(b) Warranty Coverage

State Adopts	Emission Standard	Calibration Gas Concentration*
Warranty Emission Standards of	200 ppm C6 HC 1.0% CO	200 ppm C3 - 800 ppm C3 .5% CO - 2.0% CO
Warranty Emission Standards of	220 ppm C6 HC 1.2% CO	220 ppm C3 - 880 ppm C3 .6% CO - 2.4% CO
State Emission Standards of	400 ppm C6 HC 4.0% CO	200 ppm C3 - 800 ppm C3 1.0% CO - 4.0% CO

* Note: Standard is expressed in ppm hexane (C6). Span gases are expressed as ppm propane (C3) assuming an approximate correction factor of 0.5.

2.3.2 State Requirements

In addition to meeting the Warranty requirements for propane and CO calibration gas concentrations, some states may wish to use other concentrations of propane and CO in performing multipoint calibrations on analyzers used in the I/M programs. Also, some states may wish to use CO_2 in multipoint calibrations also. In these cases the state would need several cylinders of propane, CO and/or CO_2 calibration gas at varying concentrations, all with accuracies of $\pm$2% to NBS standards for best results. For these reasons, we have designed the Recommended Practice in such a way that a gas manufacturer can demonstrate traceability for any ordered gas concentration which falls between the range of NBS standard reference material concentrations discussed in Section 2.4 (see Table 3). I/M calibration gas

concentrations ordered either above the highest standard or below the lowest standard listed in Table 3 are not assured traceability ±2% to NBS standards within the scope of this Recommended Practice.

2.4 NBS and Other Standards

The National Bureau of Standards tries to make available standard gases in commonly requested concentrations. Up until this year, the only NBS standards available were called Standard Reference Materials (SRM's). The concentrations of various NBS CO, propane, and CO_2 SRM's which are in the range of interest as far as I/M calibration gas is concerned are listed in Table 3. SRM's have an analytical uncertainty of ±1% to the true value of the concentration in the cylinder.

Table 3

NBS Propane, CO, and CO_2 Standards in Nitrogen
in the Concentration Range
of Typical I/M Calibration Gases

Propane NBS Standard #	Propane Concentrations
2643	100 ppm
2644	250 ppm
2645	500 ppm
2646	1000 ppm
2647	2500 ppm
2648	5000 ppm

Carbon Monoxide NBS Standard #	Carbon Monoxide Concentration
2638	5000 ppm (.5%)
2639	1.0%
2640	2.0%
2641	4.0%
2642	8.0%

Carbon Dioxide* NBS Standard #	Carbon Dioxide Concentration
2620a	1.0%
2622a	2.0%
2624a	3.0%
2626a	4.0%
1674b	7.0%
1675b	14.0%

* Other standards are available for CO_2. A list of available standards may be obtained by writing the Office of Standard Reference Materials, Chemistry Building, Room B311, National Bureau of Standards, Washington, D.C. 20234.

Historically, SRM's have been the only NBS standards. The EPA has therefore required SRM's as the standard to which calibration gases used in many mobile and stationary source programs had to be traced. This created a large demand for SRM's since the tracing process consume the SRM's. Also, the analysis procedures for SRM's are very detailed and lengthy, so SRM's have been in short supply. In an attempt to alleviate these problems associated with the lack of supply of NBS standards, the EPA Emission Monitoring and Support Laboratory at Research Triangle Park (EMSL-RTP) and NBS developed procedures that would allow gas manufacturers to make a new kind of standard, called a Certified Reference Material (CRM), which if made properly has an analytical uncertainty of about $\pm$1.3% to true value. These CRM's can be made in batch quantities, but a limitation of these CRM's is that they can be made only at SRM concentrations.

The analytical procedures described in this report rely on there being an adequate supply of NBS standards, either SRM's or CRM's. The CRM program should ensure that availability.*

Because of the difficulty in obtaining NBS standards, scientific gas manufacturers have, over the years, developed their own in-house standards which they have used in the analysis of various scientific gases. These in-house standards, called primary standards, are for the most part very

* At the time of publication of this report, one gas manufacturing company was offering CRM's for sale.

accurately named. However, there are no uniform procedures throughout the scientific gas industry for naming these standards. Therefore, differences in accuracies of primary standards between manufacturers probably exists. We mention these standards in this section because they are used by manufacturers along with NBS standards (if a gas divider is not used) to demonstrate traceability within the context of this Recommmended Practice. The NBS standards serve the function of providing a check on the accuracy of the in-house primary standards. The primary standards serve the function of providing more data points by which to construct an analyzer calibration curve than would be obtained if NBS standards were used alone.

3.0 TRACEABILITY

People familiar with the blending and naming (the affixing of a concentration label to a cylinder) of scientific gases use the word traceability to describe an analytical link between the concentration of two separate cylinders of the same kind (not necessarily the same concentration) of gas, where one of the cylinders is usually some kind of standard gas. The standards most often referred to in any traceability definition are NBS standards (these standards were discussed in section 2.4). For the purpose of this report, "traceable" will mean the use of the standards and analytical procedures discussed in this report. These procedures, if used properly, should yield an I/M calibration gas which is accurately named relative to NBS standards (either SRM's or CRM's) within ±2%, ±1.5%, or ±1%, depending on the criteria selected with the Recommended Practice. A brief discussion on how this accuracy is attained in this Recommended Practice is presented in Appendix 3.

3.1 Establishing Traceability: Overview of Procedures

The analytical procedures described in this report for establishing traceability between an I/M calibration gas and NBS standards are designed so that traceability can be demonstrated for practically any concentration of I/M calibration gas a state or I/M customer may desire to order. The general procedures are described in the body of this report. A more concise listing of the procedures is provided in Appendix 2.

Generally, the procedures for the analysis of propane, carbon monoxide, or carbon dioxide in the I/M calibration gas are dependent on the characteristics of the analysis instrumentation used to determine the concentrations of each gas. A linearity check is first conducted to determine the extent of linearity between input gas concentration and response in the instrument.* If a four-blend CO_2, CO, and propane in N_2 cylinder is to be named, an interference check is first conducted between the CO_2 and CO. If only a three-blend CO, propane and N_2 cylinder is to be made, the interference check is omitted. If instrument response during the linearity check to a given component in the subject gas is linear, a first or second order equation is developed for the instrument from analysis of six standard gases which have the same kind of component, but at different concentrations than the subject gas. This equation is used in naming the subject component in each of the I/M calibration gas cylinders. If the instrument has a non-linear response to a given component in the subject gas, a third or fourth order equation is developed for the instrument from analysis of eight standard gases which have the same kind of component, but again at different concentrations than the subject gas. The equation is then used in determining the concentration of the subject component in each of the I/M calibration gas cylinders.

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* Although there are exceptions to the rule, the instrumentation most commonly used to analyze carbon monoxide and carbon dioxide (usually Non-Dispersive Infrared-NDIR-analyzer) is non-linear, while instrumentation commonly used to analyze propane (usually a Flame Ionization Detector-FID) is linear.

Before presenting details of the analysis procedures, discussions of the analysis of pure components used in the blending process and the selection of cylinders used to hold I/M calibration gas are presented.

3.2 Analysis of Pure Components

Scientific gas manufacturers must follow certain procedures in ordering and analyzing pure components used to make I/M calibration gas. First, the nitrogen used as diluent in the calibration gas must be 99.99% pure nitrogen to comply with this Recommended Practice. This grade of nitrogen is readily available at a reasonable cost and is frequently used in blending scientific gases. An analysis does not have to be performed on the nitrogen. Propane used must be "instrument grade" propane which is certified to be 99.5% propane, and the balance will be other hydrocarbons (e.g., methane, iso-butane, butane and ethane). An analysis must be performed of this bulk propane to determine in fact that the propane gas used is at least 99.5% propane. This analysis can be easily performed with a Gas Chromatograph (GC) which is appropriately fitted to read propane. Lastly, the carbon monoxide used must have a methane count of less than 100 ppm, and the carbon dioxide used must have a total hydrocarbon (THC) count of less than 100 ppm.

Although these specifications for the pure components might seem moderately stringent when one considers that the dilution of the propane, carbon monoxide and carbon dioxide with nitrogen will result in these trace components (particularly methane) having very little effect on the resultant accuracy of the I/M span gas, they nonetheless contribute to error in naming the I/M

calibration gas and should be limited. Also, the small extra cost of the components ordered and analyzed to these specifications will have virtually no effect on the overall cost of making the I/M calibration gas. The bulk of the cost in making an I/M calibration gas is incurred in filling and analyzing the final blend.

3.3 Cylinders

Any size disposable or reusable cylinder may be used as a container for I/M calibration gas named according to this Recommended Practice, however, the cylinders must be constructed of either steel or aluminum. Also, reusable cylinders must be fitted with CGA-350 valves (CGA stands for the Compressed Gas Association). Disposable cylinders must be fitted with a CGA 1/4-inch flare-fitting valve. The use of these valves only will not be a burden to gas manufacturers, and they will allow I/M calibration gas users to switch suppliers (gas manufacturers) without having to purchase new regulators.

I/M calibration gas users should be aware that the analysis of each cylinder of I/M calibration gas contributes a significant portion to the ultimate price of the calibration gas. It probably costs no more for a manufacturer to perform an analysis of a large cylinder than to perform an analysis on a small cylinder (except in the case of calibration gas sold in disposable containers, where special abbreviated analysis procedures are allowed). Therefore, the cost per cubic foot of calibration gas sold in a large cylinder will likely be significantly less than the cost per cubic foot of calibration gas in a small cylinder.

3.4 Instrument Preparation and Calibration

3.4.1 Definition of Linearity

The NBS standard reference materials (either SRM's or CRM's) listed in Table 4 or a gas divider which can be used to dilute the highest concentration standard to at least three lower concentrations which match within ±5% the standard concentrations, and a instrument grade 99.99% pure nitrogen cylinder, must be used to determine instrument linearity. For the purposes of these analytical procedures, a linear analytical instrument is defined as one which yields three intermediate points in the range of 1.0% CO to 8.0% CO, 250 ppm propane to 2500 ppm propane and/or 1.0% CO_2 to 7.0% or 14.0% CO_2 which deviate by ±2% of point* or less from a straight line drawn from the point determined by the zero gas to the highest calibration point. To be considered linear, the difference between the concentrations indicated by the intermediate points and the straight line must not exceed ±2% of the concentration values of the intermediate points. The range of allowable deviations from the straight line are illustrated in Table 4.

The reader will note that linearity is defined only between endpoints which coincide with available NBS standards which are in the range of interest for I/M calibration gases (see Table 4). This range in which linearity is defined is wide enough to accomodate practically any concentration of I/M calibration gas ordered by a state or I/M area.

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* ±2% of point is ±2% of reading. For example, if a reading of a certain gas is 6.0% CO, ±2% of 6.0% CO is ±.12% CO.

Table 4

NBS Standards Used to Determine Instrument Linearity*

Propane in N_2	Allowable Deviations For Linear Instruments
250 ppm	±5 ppm
500 ppm	±10 ppm
1000 ppm	±20 ppm
2500 ppm	±50 ppm
CO in N_2	
1.0%	±.02% CO
2.0%	±.04% CO
4.0%	±.08% CO
8.0%	±.16% CO
CO_2 in N_2	
1.0%	± .02% CO_2
3.0%	± .06% CO_2
4.0%	± .08% CO_2
7.0%	± .14% CO_2
14.0%**	± .28% CO_2

* An instrument-grade 99.99% pure nitrogen cylinder must also be used to establish the instrument zero.

** This CO_2 standard must be used in the linearity check if the CO_2 concentration to be named is over 7.0%. The 1.0% CO_2 standard can be dropped from the check in this situation.

Linearity need only be determined once on a particular instrument, unless service is performed on the instrument, in which case the linearity check must be conducted after service is completed.

3.4.2 CO_2 Interference Check

The following check is to be made only if CO is to be named in a cylinder that also contains CO_2. Otherwise, this step shall be omitted.

Carbon dioxide gas (with nitrogen as a diluent) at the same concentration which is to be used in the I/M calibration cylinder must be analyzed with the CO analysis instrumentation. The response of the CO analyzer to CO_2 must be less than .5% of the concentration of CO which is to be used in the I/M calibration cylinder.

3.4.3 Calibration Curve for Linear Instruments

Prior to the analysis of each batch of I/M calibration gas, a calibration curve must be generated on the range that is to be used to analyze the I/M calibration gas. No more than one hour must elapse between the time at which the calibration curve is generated and the start of the analysis of the batch of I/M calibration gas begins. If analysis of a portion of the batch is postponed for two hours or more, a completely new calibration curve must be generated.

A minimum of six cylinders must be used to generate the calibration curve. One cylinder must be instrument grade 99.99% pure nitrogen, two other cylinders must be undiluted NBS standards which are above and below the concentration of the I/M calibration gas to be named, and the other three cylinders can be primary standards or gases obtained by using a gas divider to dilute either NBS standard. Instrument responses for the five points other than the zero point should be approximately equally spaced on the range of the instrument which is to be used to name the I/M calibration gas. For example, if a 3.0% CO I/M calibration gas is to named, instrument resonses could be obtained at 1.0% CO, 2.5% CO, 4.0% CO, 6.5% CO, and 8.0% CO. The 1.0% and 8.0% CO could be NBS standards, with the others being either primary standards or diluted NBS standards.

A first or second order equation must be calculated from the instrument response for the six gases. If the difference between any point and the first or second order curve is less than $\pm$1.0% for gases intended to be traceable $\pm$2% to NBS ($\pm$.5% if gases traceable $\pm$1% to NBS are to be named or if CO is to be named in a cylinder containing CO_2), the first or second order equation thereby derived may be used to name I/M calibration gases in this Recommended Practice. Inability to satisfy this criteria with a first or second order equation is an indicator of improperly named primary standards, a malfunctioning gas divider, and/or malfunctioning analysis instrumentation. Rectifying these problems will likely result in the criterion being satisfied.

It is suggested that if a first-order equation yields a calibration line which meets the above criteria, but calibration points do not appear to be randomly distributed above or below the line (i.e., there is a cluster of nearby points above the line and another cluster below), then a second-order equation should be generated from the calibration points. This will increase the accuracy of the I/M calibration gas naming process. The second order curve must meet the ±1.0% of point (±.5% if gases traceable ±1% to NBS are to be named or if CO is to be named in a cylinder containing CO_2) criterion stated in the previous paragraph.

3.4.4 Calibration Curve for Non-Linear Instruments

Prior to the analysis of each batch of I/M calibration gas with a non-linear instrument, a calibration curve must be constructed on the range that is to be used in analyzing the I/M calibration gas. No more than one hour must elapse between the time at which the calibration curve is generated and the start of the analysis of the batch of I/M calibration gas begins. If analysis of a portion of the batch is postponed for two hours or more, a completely new calibration curve must be generated.

A minimum of eight cylinders must be used to construct the calibration curve. One cylinder must be instrument-grade 99.99% pure nitrogen, two other cylinders must be undiluted NBS standards which are above and below the concentration of the I/M calibration gas to be named, and the other five cylinders can be primary standards or gases obtained by using a gas divider to dilute either NBS standard. Instrument responses for the seven points other

than the zero point should be approximately equally spaced on the range which is to be used to name the I/M calibration gas.

A third or fourth-order polynomial equation must be calculated from the instrument responses to the eight gases obtained during the calibration step.

No inflection points are allowed in the equation of the curve generated from analysis of the eight gases.* If an inflection point occurs in a fourth-order equation, a third-order equation should be tried. If the differences between any point and the curve is less than ±1.0% for gases intended to be traceable ±2% to NBS (±.5% if gases traceable ±1% to NBS are to be named or if CO is to be named in a cylinder containing CO_2), the equation thereby developed may be used to name I/M calibration gases in this Recommended Practice. Inability to satisfy these criteria with a third or fourth-order equation is an indicator of improperly named primary standards, a malfunctioning gas divider, and/or malfunctioning analysis instrumentation.

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* Inflection points can be determined by taking the second derivative of the resultant calibration curve equation, setting it equal to zero, and evaluating over the range of 0 to 100% full scale on the given range.

It is suggested that if a third-order equation yields a calibration curve which meets the above criteria for non-linear instruments, but calibration points do not appear to be randomly distributed above or below the curve (i.e., there is a cluster of nearby points above the curve and another below the curve), then a fourth-order equation should be generated from the calibration points. This will increase the accuracy of the I/M calibration gas naming process. However, no inflection points are allowed in this fourth-order curve. The fourth-order curve must meet the ±1% of point (±.5% if gases traceable ±1% to NBS are to be named or if CO is to be named in a cylinder containing CO_2) criterion stated in the previous paragraph.

3.5 Analysis of I/M Calibration Gas Cylinders

3.5.1 Re-Usable Cylinders

After valid calibration curves are obtained for all instruments that are to be used to analyze the I/M calibration gas, the analysis of I/M calibration gas can begin. Each component (with the exception of the diluent) of every re-usable I/M calibration gas cylinder must be discreetly analyzed. I/M calibration gas cylinders can be analyzed in any sequence, however, the highest concentration NBS standard used to generate the calibration curve and the zero gas cylinder must be repeated after every ten analyses of I/M calibration gas cylinders to ensure that substantial instrument zero or span drift has not occurred which could detrimentally affect the I/M calibration gas naming process. No analyzer adjustments are permitted during the naming process. Zero and span drifts are calculated as a percentage of full scale.

They are added together to arrive at a total drift error. If the total drift error changes by more than ±1.0% (±.5% if gases traceable ±1% to NBS are to be named or if CO is to be named in a cylinder containing CO_2 to ±1.5% to NBS) throughout the analysis process, a new calibration curve must be constructed for the analyzer in accordance with the procedures described in section 3.4.2 or 3.4.3, and the analyses of the previous ten cylinders of I/M calibration gas must be repeated.

3.5.2 Disposable Cylinders

It is likely that much of the I/M calibration gas sold to I/M users will be in the form of disposable cylinders. Many analyzer manufacturers are designing the stands that hold their analyzers to include a holder for a disposable cylinder that can be used to periodically calibration-check the analyzer. These disposable cylinders hold a small amount of calibration gas, usually 6 to 10 cubic feet. The disposable cylinders are likely to be used predominantly in licensed facilities of decentralized programs, where (1) there may be no room for a large cylinder of I/M calibration gas, or (2) the facility owner does not want to incur the higher initial cost of a larger cylinder. Fewer vehicles will be inspected on the basis of each disposable cylinder.

As stated previously, for re-usable cylinders the Recommended Practice requires that an analysis be performed according to the prescribed techniques on each component (with the exception of the diluent) in every cylinder. However, the result of insisting on this requirement for disposable cylinders

also might be to make them prohibitively expensive for small facilities in decentralized programs.

Disposable cylinders are usually filled in one of two ways: (1) they can be filled one-by-one from a re-usable cylinder or bulk homogeneous mixture, or (2) separate cylinders of pure components can be piped together and connected to a common manifold to which the empty disposable cylinders are also connected, thereby filling the disposable cylinders simultaneously from a single stream of "dynamically" blended gases. In this latter filling process, the blend is usually continuously analyzed while the disposable cylinders are being filled. In the first filling process mentioned, all components of the mixture have usually been analyzed already. In both filling processes mentioned, analysis is usually performed on the gas blend somewhere along its path to the disposable cylinder, which makes the probability of the mixture in the disposable cylinder being accurate much greater than if an analysis of the blend entering a disposable cylinder had not been performed. However, blunders (cylinders with contents significantly different than the labeled concentrations) can still occur with the disposable cylinders, particularly where a disposable cylinder is not properly evacuated prior to filling, or a disposable cylinder is not properly filled because of some malfunction in the ganging hardware.

For these reasons, this Recommended Practice requires only that an analysis be performed on (1) <u>one</u> component of <u>each</u> filled disposable cylinder, and on (2) the other components (with the exception of the diluent) in 10% and no less

than ten* total cylinders of the filled disposable cylinders that have been blended with a continuous analysis system or filled from a previously blended and analyzed bulk mixture. The mean concentration of the first component which is analyzed in all disposable cylinders in the batch is calculated. If the concentration of the first component is any cylinder in the batch is more than ±2% different from the mean concentration, that cylinder must have all components discreetly analyzed. Any cylinder whose first component concentration is within ±2% of the mean concentration of the batch may apply the criterion of the following paragraph in the determination of the concentration of other components in that cylinder.

The mean concentration of the other component in the 10% sample(s) are calculated. The standard deviation of the concentration values of the other components in the 10% samples must be less than or equal to ±.5% of each sample's mean.** If they are, all cylinders in the batch shall be labeled with the mean concentrations of the other components in the 10% samples. If they are not, an analysis of all cylinders for the other components is required.

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* If less than 10 disposable cylinders are to be named, all components (except the diluent) must be analyzed in each cylinder.

** This will assure that 95% of the sample will be within ±1% of the mean concentration (±2 standard deviations), and 99% of the sample will be within ±2% of the mean concentration (±4 standard deviations). For an explanation of this statistical criteria see Appendix 4.

If a continuous analysis system for all components (propane, CO and CO_2) has not been used in the case where disposable cylinders are filled from pure components flowing through a common manifold, or where an analysis has not been performed on each component in the bulk mixture in the case where disposable cylinders are filled from the bulk mixture, an analysis must be done on each component of every disposable cylinder.

3.6 Calculating I/M Calibration Gas Concentrations

3.6.1 Equations Used

Linear Instruments - The concentration of each component of an I/M calibration gas (propane and CO) that has been analyzed with a linear instrument shall be determined by the first or second order equation generated by the calibration curve as discussed in Section 3.4.2.

Non-Linear Instruments - The concentration of components in I/M calibration gas analyzed with a non-linear instrument shall be calculated by the third or fourth-order calibration curve equation discussed in section 3.4.3.

3.6.2 Concentration Determination

Re-Usable Cylinders - Propane, carbon monoxide, and CO_2 if used are analyzed in each re-usable cylinder of I/M calibration gas blended. The labeled concentration of each component in each cylinder must be calculated from the meter responses for each component using the equations specified in Section 3.6.1.

Disposable Cylinders - For disposable cylinders in which each component has been analyzed in all cylinders of a batch (see Section 3.5.2), the same rules apply for determining the concentration label of each component as apply for re-usable cylinders (see previous paragraph). For disposable cylinders in which one component has been analyzed in every cylinder, while the other components have been analyzed in 10% (and not less than 10) of the cylinders of the batch, the concentration label of the first component shall be calculated separately from the meter response of each cylinder using the equations specified in Section 3.6.1. The concentration label for the other components on all cylinders shall be the mean concentration values of the 10% samples, provided all other conditions in Section 3.5.2 have been met.

3.7 Cylinder Labeling and Documentation

All I/M calibration gas cylinders named according to these procedures must be labeled with a tag which contains at a minimum the following information:

(i) Cylinder number, except in the use of disposables, where the batch number is required

(ii) Concentration of propane (in ppm), CO (in mol%), and CO_2 (in mol%) in cylinder gas (determined from Section 3.6.2), and accuracy specification (i.e., $\pm$2%, $\pm$1.5% or $\pm$1.0%)

(iii) Balance gas

(iv) Analysis date

(v) Cylinder numbers of NBS standards used in determining instrument calibration curves

(vi) Vendor name

(vii) The statement that "This gas has been named in accordance with the EPA Recommended Practice for Naming I/M Calibration Gas".

The gas manufacturer must retain calibration curve data on each batch analysis of I/M calibration gas for a minimum period of two years.

3.8 Audits of I/M Calibration Gases

A formal audit of I/M calibration gas which has been named according to this practice is not necessary prior to the sale and delivery of the I/M calibration gases. However, it should be remembered that state auditors in decentralized I/M programs will likely be checking on a monthly basis the accuracies of calibration gases used with inspection analyzers. Facilities with improperly labeled calibration gases will likely be required by auditors to suspend the conducting of inspections until the problem with their calibration gas is resolved. The labeling requirements of the Recommended Practice should assist all concerned parties in determining why a cylinder or group of cylinders was improperly labeled.

The EPA may, from time-to-time, conduct audits of I/M calibration gas by acquiring cylinders named according to the Recommended Practice on the open market and analyzing these cylinders. The results of such audits are likely to be published by the EPA for the benefit of I/M programs.

APPENDICES

Appendix 1

Emission Performance Warranty Regulations Pertaining to I/M Calibration Gases

§ 85.2217 Calibrations, adjustments.

(a) Equipment shall be calibrated in accordance with the manufacturers' instructions.

(b) Within one hour prior to a test, the analyzers shall be zeroed and spanned. Ambient air is acceptable as a zero gas; an electrical span check is acceptable. Zero and span checks shall be made on the lowest range capable of reading the short test standard.

(c) Within eight hours prior to a loaded test, the dynamometer shall be checked for proper power absorber settings.

(d)(1) The analyzers shall have been spanned and adjusted, if necessary, using gas traceable to NBS standards ± 2% within one week of the test. These span gases shall have concentrations either:

(i) Between the standards specified in this subpart and the jurisdictions inspection standards for 1981 model year light duty vehicles, or

(ii) Be within −50% to +100% of the standards in this subpart.

(2) For analyzers with a separate calibration or span port, CO readings using calibration gas through the probe and through the calibration port shall be made; discrepancies of over 3% shall require repair of leaks. No analyzer adjustments shall be permitted during this check.

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Appendix 2

Listing of Analysis Requirements

for Recommended Practice

Step 1 Analysis of Pure Components : Analyze pure propane used to blend I/M calibration gas for other hydrocarbons such as methane, iso-butane, butane and ethane. Analyze pure carbon monoxide for methane. Analyze the pure CO_2 (if used) for total hydrocarbons. These analyses are not necessary prior to the blending of each batch of I/M calibration gas, but should be performed sometime prior to the blending of the first I/M calibration gas batch made from newly received pure components.

Acceptance Criteria: The total "other" hydrocarbon count of pure propane (i.e., excluding propane) must be less than .5%. The methane count of pure carbon monoxide must be less then 100 ppm. The total hydrocarbon count of the CO_2 must be less than 100 ppm.

Step 2 Determination of Insrument Linearity : Determine whether instrument(s) to be used in analysis of I/M calibration gas is (are) linear or non-linear. The following NBS standards (either CRMs or SRMs) must be used in determining linearity, or a gas divider may be used with the highest concentration standards (i.e., 2500 ppm propane in N_2, 8.0% CO in N_2 or 14.0% CO_2 in N_2) listed below to

obtain three points below the highest concentration standard. If a gas divider is used, the lower points should be targeted to within ±5% of the concentration of the standards listed in the table. An instrument grade 99.99% pure nitrogen must be used to establish the instrument zero. The 14.0% CO_2 standard must be used in the linearity check if the CO_2 concentration in the I/M calibration gas to be named is over 7.0% CO_2. The 1.0% CO_2 standard can be dropped from the check in this situation.

NBS Standards Used to Determine
Instrument Linearity

Propane in N_2	Allowable Deviations For Linear Instruments
250 ppm	± 5 ppm
500 ppm	±10 ppm
1000 ppm	±20 ppm
2500 ppm	±50 ppm
CO in N_2	
1.0%	±.02% CO
2.0%	±.04% CO
4.0%	±.08% CO
8.0%	±.16% CO
CO_2 in N_2	
1.0%	±.02% CO_2
3.0%	±.06% CO_2
4.0%	±.08% CO_2
7.0%	±.14% CO_2
14.0%	±.28% CO_2

Acceptance Criteria: The criteria for determining instrument linearity is as follows. A linear analytical instrument is defined as one which yields three intermediate points in the range of 1.0% CO to 8.0% CO, 250 ppm propane to 2500 ppm propane, and/or 1.0% CO_2 to 7.0% CO_2 or 14.0% CO_2, (depending on the CO_2 concentration to be named) which deviate by ±2% of point or less from a straight line drawn from the point

determined by zero gas to the highest calibration point. To be considered linear, the difference between the concentrations indicated by the intermediate points and the straight line must not exceed ±2% of the concentration values of the intermediate points. The range of allowable deviations from the straight line is illustrated in the table above. Instruments not meeting this criteria are classified as non-linear instruments for the purpose of this Recommended Practice.

Step 3: CO_2 Interference Check : The following check is to be made only if CO is to be named in an I/M calibration cylinder that also contains CO_2, otherwise this step shall be omitted.

CO_2 gas (with nitrogen as a diluent) at the same concentration which is to be used in the I/M calibration cylinder must be analyzed with the CO analysis instrumentation.

Acceptance Criteria: The response of the CO analyzer to CO_2 must be less than .5% of the concentration of CO which is to be used in the I/M calibration cylinder.

Step 4: Generation of Calibration Curve for Linear Instruments : Prior to the analysis of each batch of I/M calibration gas, a calibration curve must be generated on the range that is to be used to analyze the I/M calibration gas. No more than one hour must elapse between the time at which the calibration curve is generated and the start of the analysis of the batch of calibration gas begins. If analysis of a portion of the batch is postponed for two hours or more, a completely new calibration curve must be generated.

A minimum of six cylinders must be used to generate the calibration curve. One cylinder must be instrument grade 99.99% pure nitrogen, two other cylinders must be undiluted NBS standards which are above and below the concentration of the I/M calibration gas to be named, and the other three cylinders can be primary standards or gases obtained by using a gas divider to dilute either NBS standard. Instrument responses for the five points other than the zero point should be approximately equally spaced on the range of the instrument which is to be used to name the I/M calibration gas. For example, if a 3.0% CO I/M calibration gas is to named, instrument resonses could be obtained at 1.0% CO, 2.5% CO, 4.0% CO, 6.5% CO, and 8.0% CO. The 1.0% and 8.0% CO could be NBS standards, with the others being either primary standards or diluted NBS standards.

A first or second order equation must be calculated from the instrument response for the six gases.

Acceptance Criteria: If the difference between any point and the first or second order curve is less than ±1.0% for gases intended to be traceable ±2% to NBS (±.5% if gases traceable ±1% to NBS are to be named or if CO is to be named in a cylinder containing CO_2), the first or second order equation thereby derived may be used to name I/M calibration gases in this Recommended Practice. Inability to satisfy this criterion with a first or second order equation is an indicator of improperly named primary standards, a malfunctioning gas divider, and/or malfunctioning analysis instrumentation. Rectifying these problems will likely result in the criteria being satisfied.

It is suggested that if a first-order equation yields a calibration line which meets the above criteria, but calibration points do not appear to be randomly distributed above or below the line (i.e., there is a cluster of nearby points above the line and another cluster below), then a second-order equation should be generated from the calibration points. This will increase the accuracy of the I/M calibration gas naming process. The second order curve must meet the ±1.0% of point (±.5% if gases traceable ±1% to NBS are to be named or if CO is to be named in a cylinder containing CO_2) criterion stated in the previous paragraph.

Step 5: Generation of Calibration Curve for Non-Linear Instruments : Prior to the analysis of each batch of I/M calibration gas with a non-linear instrument, a calibration curve must be constructed on the range that is to be used in analyzing the I/M span gas. No more than one hour must elapse between the time at which the calibration curve is generated and the start of the analysis of the batch of I/M calibration gas begins. If analysis of a portion of the batch is postponed for two hours or more, a completely new calibration curve must be generated.

A minimum of eight cylinders must be used to construct the calibration curve. One cylinder must be instrument-grade 99.99% pure nitrogen, two other cylinders must be undiluted NBS standards which are above and below the concentration of the I/M calibration gas to be named, and the other five cylinders can be primary standards or gases obtained by using a gas divider to dilute either NBS standard. Instrument responses for the seven points other than the zero point should be approximately equally spaced on the range which is to be used to name the I/M calibration gas.

A third or fourth-order polynomial equation must be calculated from the instrument responses to the eight gases obtained during the calibration step.

Acceptance Criteria: No inflection points are allowed in the equation of the curve generated from analysis of the eight gases.* If an inflection point occurs in a fourth-order equation, a third-order equation should be tried. If the differences between any point and the curve is less than ±1.0% for gases intended to be traceable ±2% to NBS (±.5% if gases traceable ±1% to NBS are to be named or if CO is to be named in a cylinder containing CO_2), the equation thereby developed may be used to name I/M calibration gases in this Recommended Practice. Inability to satisfy these criterion with a third or fourth-order equation is an indicator of improperly named primary standards, a malfunctioning gas divider, and/or malfunctioning analysis instrumentation.

It is suggested that if a third-order equation yields a calibration curve which meets the above criteria for non-linear instruments, but calibration points do not appear to be randomly distributed above or below the curve (i.e., there is a cluster of nearby points above the curve and another below the curve), then a fourth-order equation should be generated from the calibration points. This will increase the accuracy of the I/M calibration gas naming process. However, no inflection points are allowed in this fourth-order curve. The fourth-order curve must meet the ±1% of point (±.5% if gases traceable ±1% to NBS are to be named or if CO is to be named in a cylinder containing CO_2) criterion stated in the previous paragraph.

Step 6A : Steps 5A and 5B differ in that Procedure A is for analysis of re-usable cylinders, and Procedure B is for analysis of disposable cylinders.

Analysis of Re-Usable I/M Calibration Gas Cylinders

After valid calibration curves are obtained for all instruments that are to be used to analyze calibration gas, the analysis of I/M calibration gas can begin. Each component (with the exception of the diluent) of every re-usable I/M calibration gas cylinder must be discreetly analyzed. I/M calibration gas cylinders can be analyzed in any sequence, however, the highest concentration NBS standard used to generate the calibration curve and a zero gas cylinder must be repeated after every ten analyses of I/M calibration gas cylinders to ensure that substantial instrument zero or span drift has not occurred which could detrimentally affect the I/M calibration gas naming process. No analyzer adjustments are permitted during the naming process. Zero and span drifts are calculated as a percentage of full scale. They are added together to arrive at a total drift error.

Acceptance Criteria: If the total drift error changes by more than ±1.0% (±.5% if gases traceable ±1% to NBS are to be named or if CO is to be named in a cylinder containing CO_2 to ±1.5% to NBS) throughout the analysis process, a new calibration curve must be constructed for the analyzer and the analyses of the previous ten cylinders of I/M calibration gas must be repeated.

Step 6B : Analysis of Disposable I/M Calibration Gas Cylinders

After valid calibration curves are obtained for all instruments that are to be used to analyze the I/M calibration gas, the analysis of I/M calibration gas can begin. For disposable I/M calibration gas cylinders, the requirement is that an analysis be performed on (1) one component of each filled disposable cylinder, and on (2) the other components, (with the exception of the diluent) on only 10% and no less than ten cylinders total of the filled disposable cylinders that have been blended with a continuous analysis system or filled from a previously blended and analyzed bulk mixture.

The mean concentration of the first component in all cylinders in the batch is calculated.

The highest concentration NBS standard used to generate the calibration curve and a zero gas cylinder must be repeated after every ten analyses of the component which is being analyzed in 100% of the disposable cylinders. No analyzer adjustments are permitted during these analysis processes.

Acceptance Criteria: If the concentration of the first component in any cylinder in the batch is more than ±2% different from the mean concentration, that cylinder must have all components discreetly analyzed.

If the total drift error does not change by more than ±1.0% (±.5% if gases traceable ±1% to NBS are to be named or if CO is to be named in a cylinder containing CO_2 to ±1.5% to NBS) throughout the analysis process, the process is valid. Changes which exceed the criteria above require that a new calibration curve must be constructed and the previous ten cylinders be re-analyzed.

For the other components in which only 10% of the batch has been analyzed, the standard deviation of the concentration values of the other components in the 10% samples must be less than or equal to ±.5% of each sample's mean. If they are, all cylinders in the batch shall be labeled with the mean concentrations of the other component in the respective 10% samples. If it is not, an analysis of all cylinders for the other components is required. If less than 10 disposable cylinders are to be named, all components except the diluent must be analyzed in each cylinder. Also, if a continuous analysis system for each component has not been used in the case where disposables are blended from pure components flowing through a common manifold, or where an analysis has not been performed on each component in the bulk mixture in the case where disposables are filled from the bulk mixture, an analysis must be done on <u>each</u> component of every disposable cylinder.

Step 7A Determination of Concentration Values for Re-Usable Cylinders	:	Steps 6A and 6B differ in their applicability for either re-usable or disposable cylinder. The labeled concentration of each component in each re-usable cylinder must be calculated from the meter responses for each component using the equations developed for the calibration curves.
Step 7B Determination of Concentration Values for Disposable Cylinders	:	For disposable cylinders in which each component has been analyzed in all cylinders of a batch, the same rules apply for determining the concentration label of each component as apply for re-usable cylinders. For disposable cylinders in which one component has been analyzed in every cylinder, while the other components have been analyzed in only 10% of the cylinders of the batch, the concentration label of the first component shall be calculated separately for each cylinder using the equations developed for the calibration curves. The concentration label for the other components in all cylinders shall be the mean concentration values of the 10% samples, provided all other conditions pertaining to the 10% samples have been met.

Step 8 Cylinder Labeling and Documentation : All I/M calibration gas cylinders named according to these procedures must be labeled with a tag which contains at a minimum the following information:

(i) Cylinder number, except in the use of disposables, where the batch number is required

(ii) Concentration of propane (in ppm) CO (in mol%), CO_2 (in mol %) in cylinder gas (determined from Section 3.6.2), and accuracy specification (i.e., $\pm$2%, $\pm$1.5% or $\pm$1.0%)

(iii) Balance gas

(iv) Analysis date

(v) Cylinder numbers of NBS standards used in determining instrument calibration curves

(vi) Vendor name

(vii) The statement that "This gas has been named in accordance with EPA Recommended Practice for Naming I/M Calibration Gas".

The gas manufacturer must retain calibration curve data on each batch analysis of I/M calibration gas for a minimum period of two years.

Appendix 3

Accuracy Discussion

The purpose of this discussion is to explain how the accuracy specifications for I/M calibration gases to NBS are derived within the Recommended Practice for I/M calibration gas filled in a re-usable cylinder. The discussion for disposable cylinders would be very similar although it would include a small statistical sampling error for components which are not analyzed in every disposable cylinder.

At certain places in the Recommended Practice small working tolerances are allowed which help make the process of naming I/M calibration gases a relatively smooth process without sacrificing a great deal of accuracy. These tolerances are limited to certain amounts so that the overall accuracy specifications can be maintained.

The maximum total error or uncertainty in a given I/M calibration cylinder can be estimated by adding together the maximum tolerances allowed from each source of error.* Of course, gas manufacturers in many cases may not use-up the maximum tolerances allowed in this Recommended Practice. But if even the worst case stack-up of tolerances meets the required accuracy specifications, all cylinders in a batch should be $\pm 2\%$ to NBS or better.

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* A certain maximum percentage error allowable in the naming process does not always translate to the same percentage error in the labeled concentration of a cylinder. In most cases the error of the labeled concentration value would be less than the error allowed in the naming process. However, for the purpose of this analysis, we have assumed that a certain percentage error allowed in the naming process translates to the same percentage error in the labeled concentration value of a cylinder.

Table 5 presents an accuracy analysis of two different types of calibration gas mixtures theoretically named by the Recommended Practice. These gases are representative of what most I/M programs will be using. The error tolerances for each source of error in the Recommended Practice are added to determine an overall accuracy (bottom of the table), which can be compared to the desired accuracy specifications at the top of the table.

Table 5

Accuracy Analysis of Two
Common I/M Calibration Gas Mixtures
Named to Different Accuracy Specifications
With the Recommended Practice

	Accuracy Spec Desired in I/M Calibration Gas of Propane, & CO in N_2		Accuracy Spec Desired in I/M Calibration Gas of Propane, CO, & CO_2 in N_2	
Error Sources	±2% to NBS	±1% to NBS	±1.5% to NBS	±2% to NBS
(1) CO_2 Interference	N/A*	N/A*	±.5%	±.5%
(2) Calibration Curves	±1%	±.5%	±.5%	±.5%
(3) Total (Zero and Span) Drift	±1%	±.5%	±.5%	±1%
Overall Accuracy (Total of 1, 2, and 3)	±2%	±1%	±1.5%	±2%

* Not appliable because this gas mixture does not contain CO_2

The reader will note that an accuracy specification of ±1% to NBS is not available in the Recommended Practice for an I/M calibration gas containing CO_2 and CO. This is because the added error of the interference between CO and CO cannot be reasonably compensated for by lowering the acceptable tolerances of the other sources of error (i.e., calibration curve and zero and span drift error). To do so would make the process of naming I/M calibration gases unduly restrictive and expensive.

Many states have specified that their auditors shall use calibration gases which are traceable ±1% to NBS, while the inspectors shall use gases which are traceable ±2% to NBS. The reasoning was that audit gas being used to pass and fail the inspector's gas should be more accurate then the inspector's gas.

From Table 5 it is apparent that auditors are not assured with this Recommended Practice of obtaining a four blend CO_2, CO, and propane in N_2 audit gas that is ±1% to NBS. Some gas manufacturers, however, may have the capability to name all components of a four-component mixture to within ±1% of NBS standards. The best specification within the scope of the Recommended Practice for the four blend mixture containing CO and CO_2 mixture is ±1.5%. Auditors either can use this gas or, if they desire ±1% gases, may (1) carry two cylinders which are ±1% to NBS, one being CO_2 in N_2, the other being CO and propane in N_2, or (2) contact a scientific gas manufacturer to discuss whether or not a four component gas mixture named ±1% to NBS standards can be supplied.

Appendix 4

Discussion of Statistical Sampling and Naming Procedure for I/M Calibration Gases Filled in Disposable Cylinders

The Recommended Practice uses statistical sampling criteria to determine whether or not an abbreviated procedure can be used in analyzing and naming I/M calibration gases filled in disposable cylinders. An example is presented below.

A batch of one-hundred disposable cylinders filled with 2.0% CO, 5.0% CO_2, and 600 ppm propane in N_2 is to be analyzed and named. The batch has been filled simultaneously from a previously analyzed bulk mixture. The following procedures illustrate the requirements of the Recommended Practice.

All one-hundred cylinders are analyzed for CO concentration. The CO labeled values are determined by the analyzer meter response to each disposable cylinder and the third or fourth order equation developed for CO. A 10% sample (with no less than 10 cylinders) is randomly selected from the batch of 100 cylinders for further analysis of CO_2 and propane. If the batch had consisted of less than one-hundred cylinders, ten cylinders would still have to be selected. For batches larger than one-hundred cylinder, 10% of the batch is required. The ten cylinders are analyzed for CO_2 and propane

concentrations. These concentrations are calculated from the analyzer meter responses to the cylinders and the equations developed for each analysis system.

The mean CO_2 and propane concentration of the sample is determined. If the mean concentration values for CO_2 and propane in the subject sample are to be used for the entire batch, the sample must display a certain amount of homogeneity. This is established by setting limits or tolerances around the mean concentration, outside of which the standard deviation of concentration values must not vary if homogeneity is assumed.

The tolerance limits set by the Recommended Practice are $\pm$.5% of the mean concentration. If the standard deviation is within these limits, one can be assured that 66% of the batch is within $\pm$.5% of the mean concentration ($\pm$1 standard deviation), 95% of the batch is within $\pm$1% of the mean concentration ($\pm$2 standard deviations) and somewhat over 99% of the batch is within $\pm$2% ($\pm$4 standard deviations) of the mean concentration. If the mean concentrations of CO_2 and propane are 4.98% CO_2 and 603 ppm, the tolerances around these values are 4.98% CO_2 $\pm$.025% CO_2, and 602 ppm $\pm$3 ppm. If the standard deviation of CO_2 and propane concentration values are within these limits, all cylinders in the batch can be labeled with these mean concentrations. If the standard deviations lie outside of these tolerances, all cylinders in the batch must be analyzed for CO_2 and propane, the concentrations of each cylinder being calculated from the analyzer meter responses to each cylinder and the equation developed for each analysis system.